

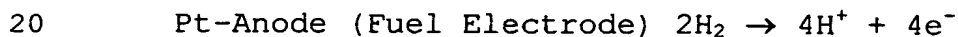
COMPOSITE ION-EXCHANGE MEMBRANES

This invention relates to a composite ion-exchange membrane and provides such a membrane per se and a method
5 of making such a membrane.

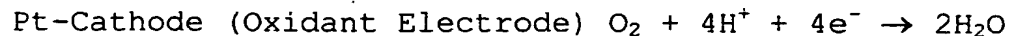
One type of known polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin
10 sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

15

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following
25 electrochemical reaction takes place:



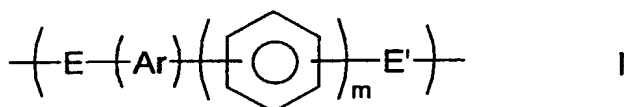
Thus, electrons and protons are consumed to produce
30 water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

The PEM 2 could comprise a single layer of ion-conducting material. However, in many cases, a single layer of material does not have satisfactory mechanical properties.

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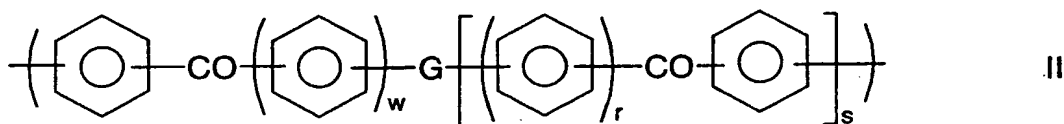
It is an object of the present invention to address the above described problem.

According to a first aspect of the invention, there is provided a composite membrane which includes a conductive polymer (i.e. an ion-conducting polymer) and a support material for the polymer, said polymer having a moiety of formula



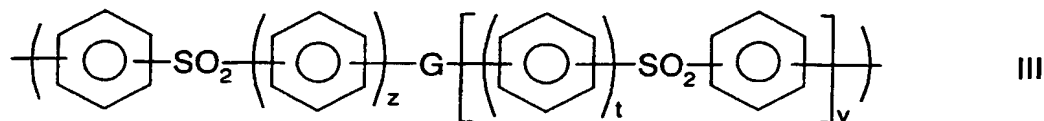
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and/or a moiety of formula



and/or a moiety of formula

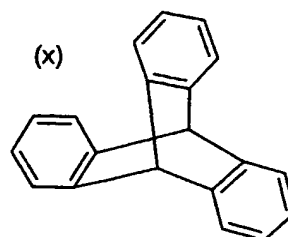
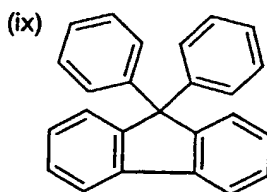
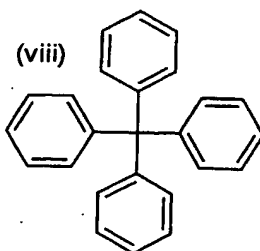
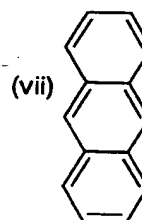
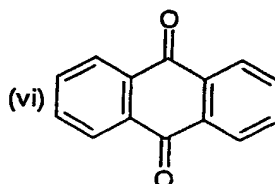
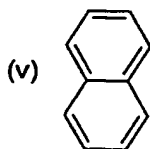
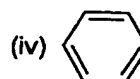
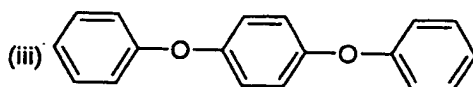
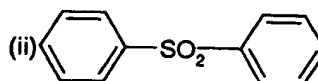
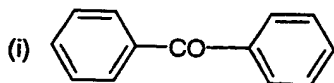
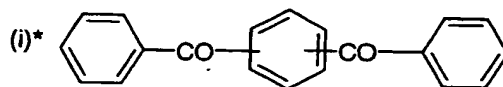
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wherein at least some of the units I, II and/or III are functionalized to provide ion exchange sites; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and

5 wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from

10 one of the following moieties (i)*, (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties



In (i)*, the middle phenyl may be 1,4- or 1,3-
5 substituted.

Preferably, said conductive polymer and said support
material do not, together, define a homogenous mixture.

10 Suitably, to provide said ion exchange sites, said
polymer is sulphonated, phosphorylated, carboxylated,

quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}_2\text{NR}_3^{20+}$ where R^{20} is an alkyl, or $-\text{CH}_2\text{NAr}_3^{x+}$ where Ar^x is an aromatic (arene), to provide a cation or anion exchange membrane.

5 Further still, the aromatic moiety may contain a hydroxyl group which can be readily elaborated by existing methods to generate $-\text{OSO}_3\text{H}$ and $-\text{OPO}_3\text{H}_2$ cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

10

Preferably, said first conductive polymer is sulphonated. Preferably, the only ion-exchange sites of said first conductive polymer are sites which are sulphonated.

15

References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{y+} , in which R^y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

25

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

30

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups
5 being bonded between units I, II, and III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine,
10 atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are C₁₋₁₀, especially C₁₋₄, alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking
15 of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

20 Another group of optional substituents of the phenyl moieties in units I, II or III include alkyls, halogens, C_yF_{2y+1} where y is an integer greater than zero, O-R^q (where R^q is selected from the group consisting of alkyls, perfluoralkyls and aryls), CF=CF₂, CN, NO₂ and OH.
25 Trifluormethylated phenyl moieties may be preferred in some circumstances.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer
30 electrolyte membrane, for example to reduce its swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be

effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described
5 in EP-A-0008895.

However, for polymers according to the invention described herein which are crystalline (which some are) there may be no need to effect cross-linking to produce a
10 material which can be used as a polymer electrolyte membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the inventions described herein may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

15

Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene
20 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

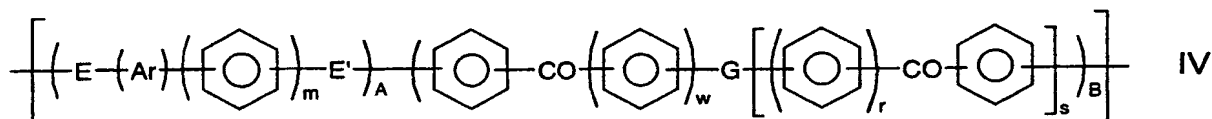
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Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;
30 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52.

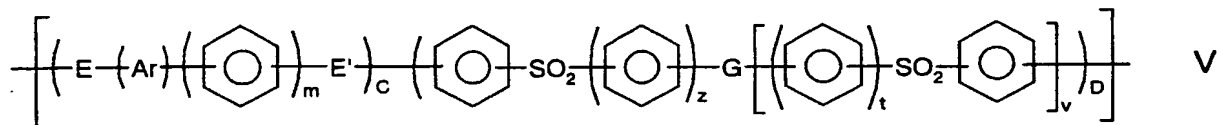
Preferably, the sum of b and c is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1.

- 5 Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about 100. Preferably, said polymer consists essentially of moieties I, II and/or III.

- 10 Said polymer may be a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula

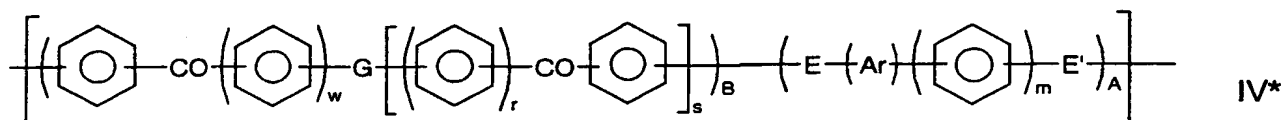


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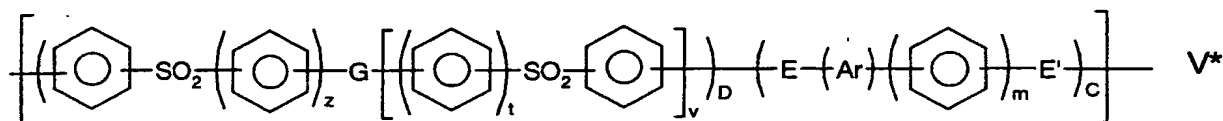
or a random or block copolymer of at least two different units of IV and/or V

- wherein A, B, C and D independently represent 0 or 1
20 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

As an alternative to a polymer comprising units IV and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula



5 or a homopolymer having a repeat unit of general formula

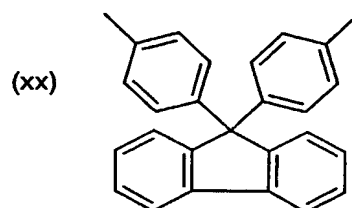
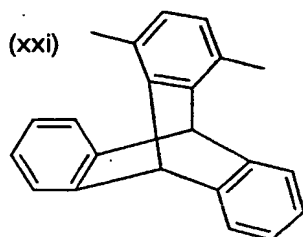
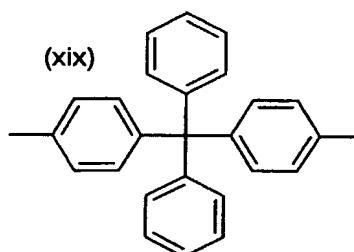
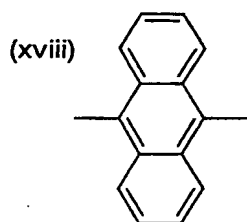
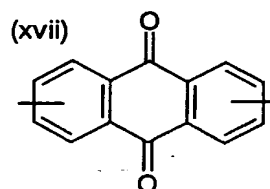
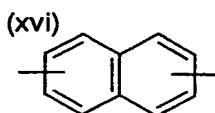
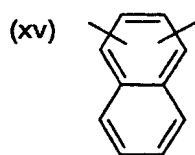
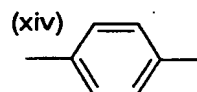
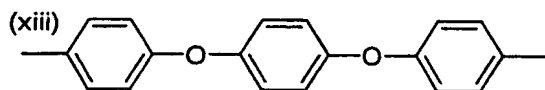
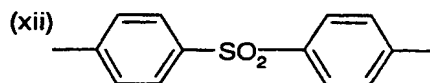
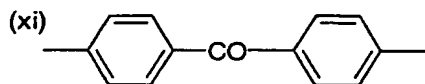
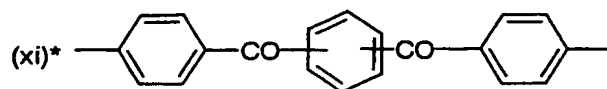


or a random or block copolymer of at least two different units of IV* and/or V*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

15 Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties
(xi)*, (xi) to (xxi):

11



In (xi)*, the middle phenyl may be 1,4- or 1,3-substituted.

Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

5

One preferred class of polymers may include at least some ketone moieties in the polymeric chain. In such a preferred class, the polymer preferably does not only include -O- and -SO₂- moieties between aryl (or other
10 unsaturated) moieties in the polymeric chain. Thus, in this case, suitably, a polymer of the first and/or second aspects does not consist only of moieties of formula III, but also includes moieties of formula I and/or II.

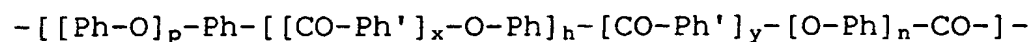
15 One preferred class of polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as described, said homopolymer or copolymer suitably includes a repeat unit of
20 general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

Referring to formula IV, preferably, said polymer is
25 not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, G represents a direct link and A and B represent 1; Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents
30 zero, w represents 1, r represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m

represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

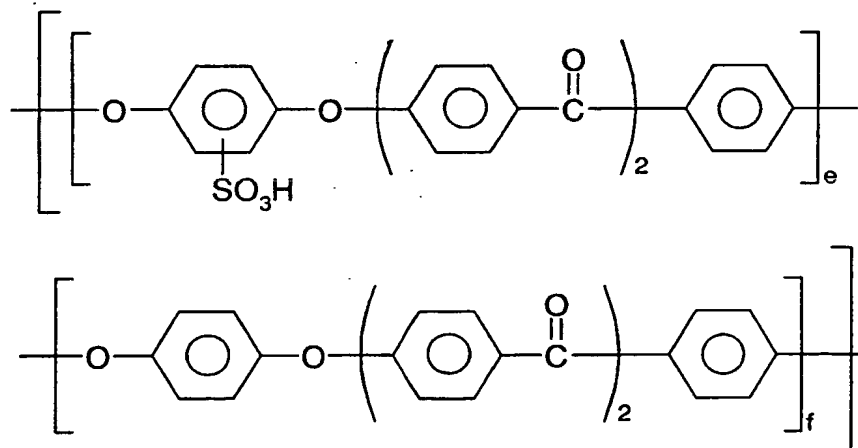
Referring to formula V, preferably, said polymer is not
 5 a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

10 Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula



15 where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

20 Preferably, said polymer does not conform to the formula



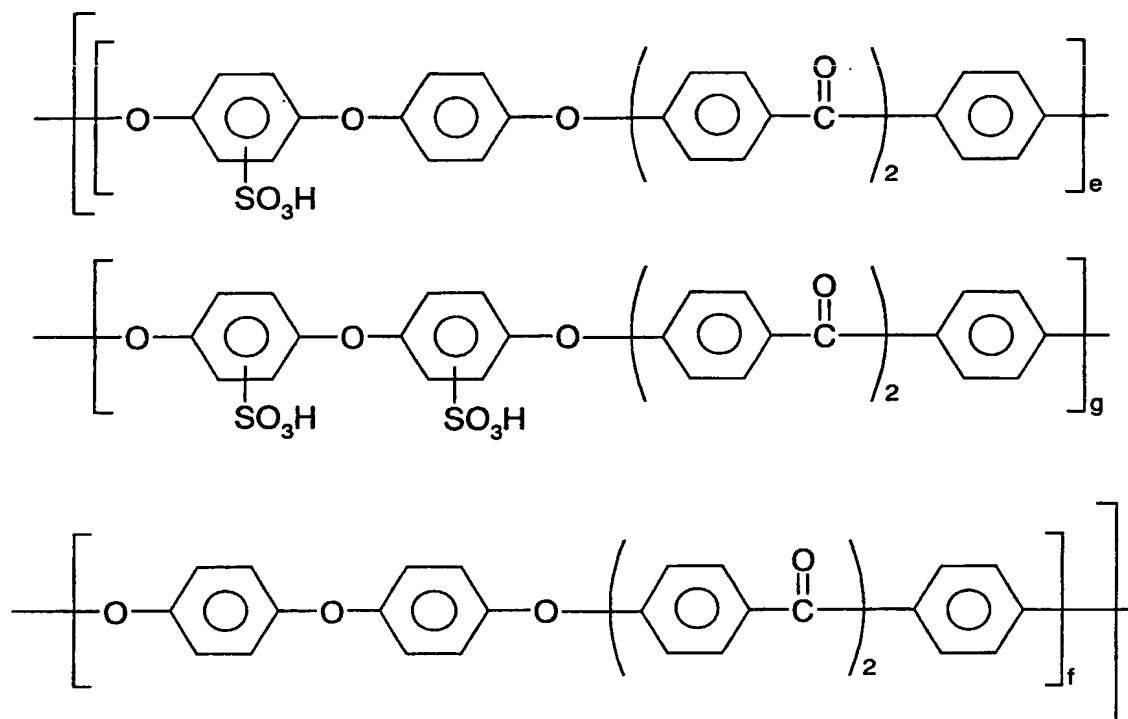
where

e is from 0.2 to 1,

f is from 0 to 0.8, and

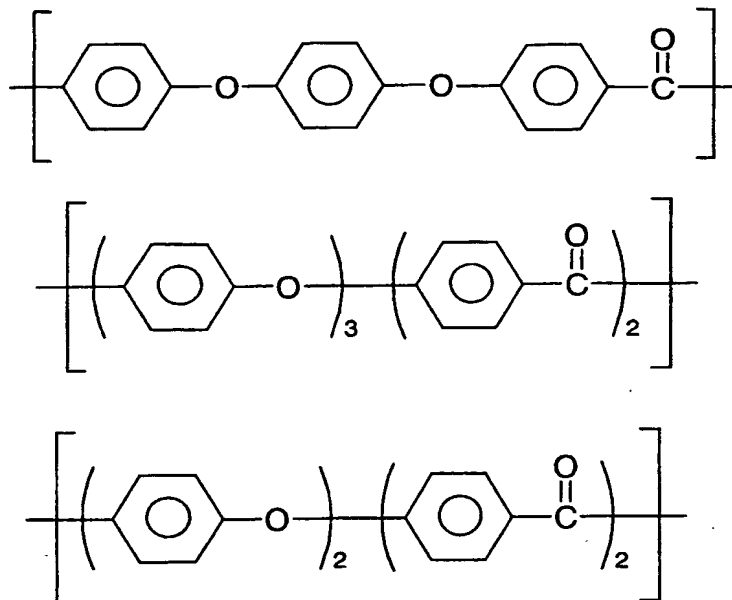
e + f = 1

Preferably, said polymer does not conform to the
5 formula



in which e is a number from 0 to 1, g is a number from
0 to 1, f is a number from 0 to 0.5, and the sum e + f + g
10 = 1.

Preferably, said polymer is not a copolymer built up
from at least two different units of formulae:



Suitable moieties Ar are moieties (i), (ii), (iv) and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative polymers comprising units IV* and/or V*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least 10π electrons in a delocalized aromatic moiety. The number of π electrons may be 12 or less.

Preferred polymers include a biphenylene moiety. Other preferred polymers include a naphthalene moiety. Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms.
5 Especially preferred polymers include a -O-biphenylene-O- moiety. Other especially preferred polymers include a -O-naphthalene-O- moiety.

Preferred polymers include a first type of moiety which
10 is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 2 hereinafter, whereas the first moiety may be substantially non-
15 sulphonatable in such a method. The use of the method of Example 2 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-\text{Ph}_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.
20 Especially preferred is the case wherein said moiety is -O- Ph_n -O- where said ether groups are para to the Ph-Ph bond.

Preferred polymers are copolymers comprising (preferably consisting essentially of) a first repeat unit
25 which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w
30 represents 1 and A and B represent 1;

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety

of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen
5 atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

Other second units which may form copolymers with any
10 of said first repeat units (a) to (e) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E
15 and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

Preferred polymers for some situations may comprise
20 first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred.

More preferred polymers are copolymers having a first
25 repeat unit selected from those described above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

Preferred polymers having repeat unit(s) of formulae
30 IV* and V* may include: a unit of formula IV* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a

repeat unit of formula V* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

5

Said polymers having repeat units IV* and V* may include any of repeat units (a) to (i) described above.

In some situations, polymers which include at least one repeat unit of formula IV or formula IV* may be preferred.

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

Preferred polymers suitably have a solubility of at least 10% w/v, (especially at least 10% w/w) preferably a solubility in the range 10 to 30% w/v (especially in the range 10 to 30% w/w) in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

5

In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl
10 moieties may be sulphonated. It is believed to be possible to sulphonate relatively easily -O-(phenyl)_n-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)_n-CO- or -O-(phenyl)_n-SO₂- may also be sulphonated at up to 100 mole% but more
15 vigorous conditions may be required. Moieties of formulae -CO-(phenyl)_n-CO- and -SO₂-(phenyl)_n-SO₂- are more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

20 The glass transition temperature (T_g) of said polymer may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the T_g may be at least 170°C, or at least 190°C or greater than 250°C or even
25 300°C.

Said polymer may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7
30 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm⁻³, said solution containing 1g of polymer per 100cm⁻³ of

solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm³, said solution containing 0.1g of polymer per 100cm³ of solution.

- 5 The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

10 The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C.

15 In general terms, said composite membrane is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

20

25 Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5µm.

30 Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least 5µm and, suitably, less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

Said support material suitably imports mechanical strength and dimensional stability to the composite membrane. The polymer may be associated with the support material to form a composite membrane in a variety of ways.

5 For example, an unsupported conductive polymer film can be preformed and laminated to the support material. Alternatively, (and preferably) the support material may be porous and a solution of the conductive polymer can be impregnated into the support material. Said support

10 material may comprise or consist essentially of an optionally-substituted polyolefin. Preferred polyolefins are optionally-substituted polyethylene and polypropylene. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene

15 or surface modified polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support

20 material has a porous microstructure of polymeric fibrils and is impregnated with said polymer throughout the material, preferably so as to render an interior volume of the membrane substantially occlusive.

25 Said support material may be made of any polymer described herein for said conductive polymer except that the polymer of said support material is either not sulphonated or otherwise functionalized to provide ion-exchange sites or is only sulphonated (or otherwise

30 functionalized to provide ion-exchange sites) at or in the region of the surface of the support material - that is, functionalisation of said support material is greater at the surface than in interior regions thereof. The EW of

said support material may be greater than 2000. Thus, said support material may comprise a polymer having moieties I, II and/or III or a homopolymer or copolymer comprising units IV and/or V.

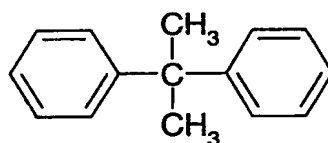
5

Preferably said support material is selected from the following homopolymers of formula IV:

- 10 - E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1
- E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m
15 represents zero, A represents 1, B represents zero
- Ar represents a moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and
20 B represent 1.
- Ar represents a structure (i)*, E represents an oxygen atom, E' represents a direct link, m represents 0, A represents 1, B represents 0.
25
- Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and
30 B represent 1

- Ar represent moiety (iv), E represents a sulphur atom, m represents 0, E' represents a direct link and B represents 0 and is selected from:
- 5 - a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:
- polysulphone for example comprising a homopolymer of
10 formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

15



Blends of the abovementioned materials may be used.

- 20 Said support material may be any support material described in W099/10165 the content of which is incorporated herein, as regards said support materials.

Said support material is preferably impregnated with
25 said conductive polymer. Said support material is preferably porous and, suitably, said conductive polymer is arranged in pores of said support material, preferably so as to render an interior volume of the support material substantially occlusive.

30

A said porous support material may be provided by a fabric which may have warp and weft strands or may comprise an irregular arrangement of fibres. Suitably, said pores are defined by the void volume of the fabric -
5 that is between the fibres. However, the fibres of the fabric themselves may be porous and penetrated by said conductive polymer. Alternatively, a said porous support material may be microporous and may suitably be made by a phase inversion process as hereinafter described. Such a
10 microporous material preferably has no through pores and/or contains no closed pores.

Preferably, said support material and said conductive polymer are in intimate contact. Whilst the two materials
15 preferably do not together define a homogeneous material, the support material and conductive polymer preferably intermingle (as would happen if, for example a surface of the support material was dissolved and contacted with said conductive material) in a boundary region between the two
20 materials.

The use of support material as described may allow polymers of lower equivalent weights (EW) (for example less than 800g/mol, less than 700 g/mol, less than 600 g/mol,
25 suitably less than 500 g/mol, preferably less than 450 g/mol or even less than 400 g/mol or 370 g/mol) or relatively inflexible and/or brittle polymers to be used as said conductive polymer in said composite membrane.

30 The composite membrane suitably includes a catalyst material (preferably a layer of a catalyst material) which is suitably a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of

the support material/conductive polymer arrangement described. Electrodes may be provided outside the catalyst material.

5 It may be preferable for each phenyl group in a conductive polymer (e.g. a sulphonated polymer) as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

10

According to a second aspect of the invention, there is provided a composite membrane which includes a conductive polymer and a support material for the polymer, wherein said polymer includes: polyaryletherketone and/or
15 polyarylethersulphone units; and units of formula $-O-Ph_n-$
 $O-$ (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

20 Preferably, each phenyl group of moiety Ph_n is sulphonated, preferably mono-sulphonated. About 100 mole% of such phenyl groups may be sulphonated as described.

Preferably, $-OPhCO-$ and/or $-OPhSO_2-$ moieties of said
25 polymer are sulphonated to a lesser extent than the phenyl groups of moiety Ph_n . Moieties $-OPhCO-$ and $-OPhSO_2-$ may be substantially non-sulphonated.

In one embodiment, said polymer may include no ketone
30 linkages and may have an equivalent weight of more than 900. Nonetheless, it has been found, surprisingly, that such polymers are still conducting.

Said composite membrane may be for a fuel cell or an electrolyser.

In addition to the utility of the composite membranes
5 described herein as ion-exchange membranes for
electrochemical fuel cells, the following further utilities
are also contemplated:

- 10 1. Proton exchange membrane based water electrolysis,
which involves a reverse chemical reaction to that
employed in hydrogen/oxygen electrochemical fuel cells.
2. Chloralkali electrolysis, typically involving the
electrolysis of a brine solution to produce chlorine
and sodium hydroxide, with hydrogen as a by-product.
- 15 3. Electrode separators in conventional batteries due to
the chemical inertness and high electrical conductivity
of the composite membranes.
4. Ion-selective electrodes, particularly those used for
the potentiometric determination of a specific ion such
20 as Ca^{2+} , Na^+ , K^+ and like ions. The composite membrane
could also be employed as the sensor material for
humidity sensors, as the electrical conductivity of an
ion exchange membrane varies with humidity.
- 25 5. Ion-exchange material for separations by ion-exchange
chromatography. Typical such applications are
deionization and desalination of water (for example,
the purification of heavy metal contaminated water),
ion separations (for example, rare-earth metal ions,
trans-uranium elements), and the removal of interfering
30 ionic species.
6. Ion-exchange membranes employed in analytical
preconcentration techniques (Donnan Dialysis). This
technique is typically employed in analytical chemical

processes to concentrate dilute ionic species to be analysed.

7. Ion-exchange membranes in electrodialysis, in which membranes are employed to separate components of an ionic solution under the driving force of an electrical current. Electrolysis applications include the industrial-scale desalination of brackish water, preparation of boiler feed make-up and chemical process water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like.
8. Membranes in dialysis applications, in which solutes diffuse from one side of the membrane (the feed side) to the other side according to their concentration gradient. Separation between solutes is obtained as a result of differences in diffusion rates across the membrane arising from differences in molecular size. Such applications include hemodialysis (artificial kidneys) and the removal of alcohol from beer.
9. Membranes in gas separation (gas permeation) and pervaporation (liquid permeation) techniques.
10. Bipolar membranes employed in water splitting and subsequently in the recovery of acids and bases from waste water solutions.

The invention extends to the use of a polymer which includes relatively easy to sulphonate units and relatively difficult to sulphonate units in the preparation of a conductive polymer for a composite membrane as described herein.

30

The conductive polymer described herein may include a blend of polymers, at least one of which is a polymer described according to the invention described herein.

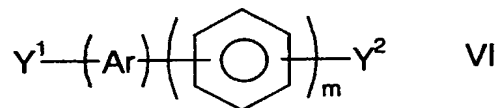
Suitably the conductive polymers herein are blended with 0-40wt%, preferably 0-20wt%, more preferably 0-10wt%, especially 0-5wt% of other polymeric materials. Preferably, however, a blend of polymers is not provided.

5

According to a third aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects. The fuel cell may
10 be a hydrogen or direct methanol fuel cell.

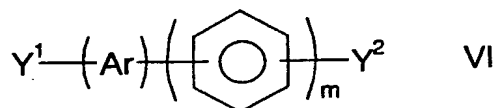
Polymers having units I, II, III, IV, IV*, V and/or V* may be prepared by:

15 (a) polycondensing a compound of general formula

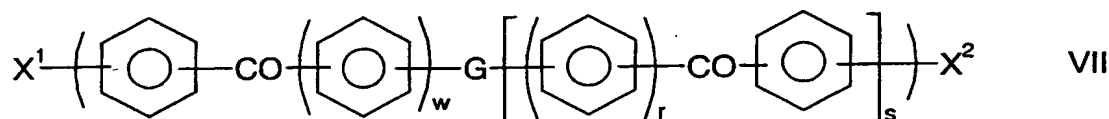


with itself wherein Y^1 represents a halogen atom or a group -EH and Y^2 represents a halogen atom or, if Y^1
20 represents a halogen atom, Y^2 represents a group E'H; or

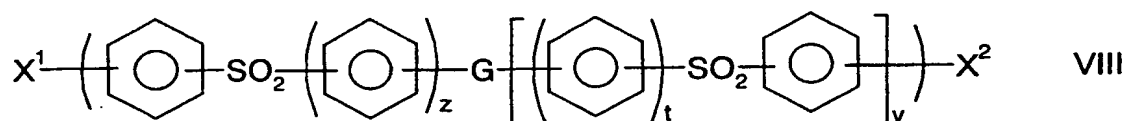
(b) polycondensing a compound of general formula



with a compound of formula



and/or with a compound of formula



5

wherein Y^1 represents a halogen atom or a group $-\text{EH}$ (or $-\text{E}'\text{H}$ if appropriate) and X^1 represents the other one of a halogen atom or group $-\text{EH}$ (or $-\text{E}'\text{H}$ if appropriate) and Y^2 represents a halogen atom or a group $-\text{EH}$ and X^2 represents the other one of a halogen atom or a group $-\text{E}'\text{H}$ (or $-\text{EH}$ if appropriate).

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after
5 polymer formation.

Preferably, where Y^1 , Y^2 , X^1 and/or X^2 represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho-
10 or para- to the halogen atom.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to
15 activating groups, especially carbonyl groups.

Wherein the process described in paragraph (a) is carried out, preferably one of Y^1 and Y^2 represents a fluorine atom and the other represents an hydroxy group.
20 More preferably in this case, Y^1 represents a fluorine atom and Y^2 represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

25 When a process described in paragraph (b) is carried out, preferably, Y^1 and Y^2 each represent an hydroxy group. Preferably, X^1 and X^2 each represent a halogen atom, suitably the same halogen atom.

30 Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate

derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be sulphonated prior to said polycondensation reaction.

Sulphonation as described herein may be carried out in concentrated sulphuric acid (suitably at least 96% w/w. preferably at least 97%w/w, more preferably at least 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

According to another aspect of the invention, there is provided a method of making a composite membrane as described herein, the method comprising causing a conductive polymer as described herein to be associated with a support material as described herein.

The conductive polymer may be associated with the support material in a variety of ways. The method may involve laminating conducting polymer and support material together. Preferably, however, the method involves
5 impregnating porous support material with said conductive polymer.

Said porous support material may be a fabric or a microporous membrane.

10

Where said porous support material is a fabric, the method may include a step of contacting the fabric with a first solvent formulation comprising a first solvent and a conductive polymer, wherein the conductive polymer is
15 preferably dissolved in the first solvent. Said fabric may, therefore, be impregnated with said formulation. Thereafter, said first solvent may be removed, leaving said conductive polymer in pores of said fabric.

20 Said first solvent and said porous support material may be selected so that said first solvent solubilises, to some degree, a surface of the support material. Said first solvent may be capable of dissolving the support material to a level of at least 5wt%. This may improve
25 contact between the conductive polymer and said support material. Optionally, said first solvent may be capable of functionalizing (e.g. sulphonating) said support material to provide ion-exchange site on a surface thereof as hereinbefore described.

30

Said first solvent may be a polar aprotic solvent, for example NMP, or may be a protic solvent. A polar aprotic solvent may not be capable of solubilising said porous

support material whereas a protic solvent may be able to solubilize and, in some cases, functionalise (e.g. sulphonate) said porous support material.

5 Where said first solvent is a protic solvent, said solvent preferably comprises or consists essentially of a strong acid solvent. Said solvent may comprise at least 90%, preferably at least 95%, more preferably at least 97%, especially at least 98% acid. Said strong acid
10 solvent may be one or more of sulphuric acid, a sulphonic acid (e.g. methane sulphonic acid, trichloromethane sulphonic acid, trifluoromethane sulphonic acid), hydrofluoric acid and phosphoric acid.

15 Preferably, a said protic first solvent comprises or consists essentially of sulphuric acid. Said solvent may include at least 96%, preferably at least 98% acid. Said solvent may include less than 99% acid. A said protic first solvent is preferably arranged to sulphonate easy to
20 sulphonate units described herein, but not difficult to sulphonate units.

In one embodiment, said fabric may be polyetheretherketone (e.g. PEEK™) and this may be
25 contacted with a formulation comprising the conductive polymer in sulphuric acid, whereby the sulphuric acid dissolves the surface of fibres of the polyetheretherketone and sulphonates it and the conductive polymer penetrates pores defined between fibres of the
30 fabric. Thereafter, phase inversion may be effected, suitably by contact with a non-solvent (e.g. water). After drying, the arrangement may be contacted with a formulation of the conductive polymer in a polar aprotic

solvent which will not substantially attack the polyetheretherketone, but may dissolve to some extent the conductive polymer already in the pores. In another embodiment, polyetherketone (e.g. PEKTM) may be used in
5 the process described instead of polyetheretherketone. In this case, the polyetherketone is dissolved by the sulphuric acid, but not surface sulphonated. Otherwise the process is as described for the treatment of polyetheretherketone.

10

In another embodiment, the first solvent may be a polar aprotic solvent (e.g. NMP) in which, suitably, a conductive material (e.g. SPEDEK/PEKES) is provided, and said support material is a material (e.g.
15 polyetheretherketone, especially PEEKTM, suitably as a fabric) which is not solubilized by said solvent, so that, suitably, the surface of said support material is not solubilized. In a further embodiment, the first solvent may be a polar aprotic solvent (e.g. NMP) in which,
20 suitably, a conductive material (e.g. SPEDEK/PEKES) is provided, and said support material is a microporous membrane suitably made of a material (e.g. polyetherketone, especially PEKTM) which is not solubilized by said solvent, so that suitably the surface
25 of said support material is not solubilized.

Where said support is a microporous membrane, preparation of the membrane may include a step of contacting a support material as described herein with a
30 solvent formulation comprising said first solvent. Said first solvent preferably solubilizes the support material. Subsequently, the method preferably includes the step of contacting the support material with a second solvent.

Said second solvent is preferably arranged to cause phase inversion. Phase inversion suitably results in said support material being rendered porous. Said second solvent is preferably a non-solvent for said support
5 material. Preferred second solvents are aqueous; especially preferred is water.

Said microporous support material is preferably contacted with said conductive polymer so that said
10 polymer penetrates into pores formed in said porous material. Said conductive polymer may be provided in a third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter,
15 the third solvent is evaporated.

Said third solvent may have the same identity as said first solvent described above. Said conductive material may be contacted with said support material in the first
20 solvent. Phase inversion may then be caused as described above which results in said conductive polymer being deposited in the pores formed by the phase inversion. After deposition of said conductive polymer in pores, as described above, the arrangement may be post-treated,
25 suitably so as to produce a substantially continuous film of said conductive polymer on the support material. Post-treatment may include the step of contacting the composite membrane which comprises conductive polymer in pores of said support material with a third solvent in which said
30 conductive polymer is relatively soluble and said support material is substantially insoluble. This may cause some dissolution of the conductive polymer in the pores resulting in film formation by coalescence of material

between pores. Optionally, a said conductive polymer may be provided in said third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter, the third solvent is evaporated.

The method may include a subsequent step of associating a catalyst material with the composite membrane prepared as described.

A said composite membrane described herein may be used in fuel cells or electrolyzers and, accordingly, the invention extends to a fuel cell or electrolyser incorporating a composite membrane as described.

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

The abbreviation NMP referred to means N-methylpyrrolidone.

PEEK™ and PEK™ are trade marks of Victrex Plc for polyetheretherketone and polyetherketone respectively.

In the specification sulphonated polyether(biphenyl)etherketone is referred to as SPEDEK;

and polyetherketoneethersulphone is referred to PEKES. Where a copolymer is followed by a ratio (e.g. SPEDEK/PEKES (1:1:5)), the ratio refers to the molar ratio of the polymeric components (e.g. the mole ratio of SPEDEK to PEKES is 1 to 1.5).

A PEM 2 may comprise a layer of an ion-conducting material in combination with a layer of a reinforcing material, as described further below.

10

Example 1

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (29.79g, 0.16 mole) 4,4'-dihydroxydiphenylsulphone (60.06g, 0.24 mole), and diphenylsulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

25

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a melt viscosity at 400°C, 1000sec⁻¹ of 0.6 kNsm⁻²; and a Tg of 188°C.

30

Example 2

The polymer of Example 1 was sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred
5 deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, ¹H nmr in DMSO-d₆ confirmed that 100 mole% of the biphenyl units had
10 sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit, giving an Equivalent Weight of 583.

15 Example 3

Membranes were produced from the polymer from Example 2 after sulphonation as described in Example 2 by dissolving the polymer in N-methylpyrrolidone (NMP) at a
20 concentration of 15% w/w. The homogeneous solution was cast onto clean glass plates and then drawn down to give 400 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

25

Example 4

The substrate, a piece of PEEK™ fabric having a thickness of 70µm and weight/unit area of 1.7x10⁻³g.cm⁻²
30 was clamped in a 10 cm diameter circular frame and immersed in a 15% (w/w) solution of SPEDEK/PEKES(1:1:5) prepared in Example 2 in NMP. The wetted substrate was placed in vacuum oven at 105°C for 1.5 hrs to remove the

NMP. The dry composite membrane was placed on a glass plate and a 50 μm thick wet coating of the solution of SPEDEK/PEKES prepared in Example 2 in NMP was applied with a Doctor Blade and dried in a vacuum oven at 105°C for 20
5 hrs to remove the NMP. The resulting composite membrane had a mean thickness of 70 μm . The weight ratio of ion-conducting membrane to PEEKTM fabric was 70:30. The unreinforced membrane of Example 3 was highly swollen and fragile after immersion in boiling water for 1 hour,
10 whereas the composite membrane was strong and flexible.

Example 5 - Comparison of Fuel Cell Performance of Reinforced Composite Membrane prepared in Example 4 with Unreinforced Membrane of Example 3.

15

The reinforced composite membrane prepared in Example 4 and the unreinforced membrane prepared in Example 3 were pre-treated by boiling in 1M sulphuric acid, allowed to cool to room temperature followed by thorough washing with
20 deionised water. Membrane Electrode Assemblies (MEA) were prepared using standard platinum loaded, Nafion® impregnated Gas Diffusion Electrodes (E-Tek, Elat 0.35mg Pt cm^{-2}) hot pressed onto the membrane, the active area being 11.8 cm^2 . The following operating conditions were
25 followed:

	Hydrogen Pressure	3Barg
	Air Pressure	3Barg
	Hydrogen Stoichiometry	1.5
30	Air Stoichiometry	3
	Cell Temperature	50°C
	Current Density	0.7A cm^{-2}

The MEA using the unreinforced membrane punctured after 30hrs, whereas the reinforced composite membrane continued operating for over 400 hrs.

5 Example 6

The substrate, a 150 mm by 130 mm piece of PEEK™ fabric as described in Example 4 was clamped to a glass plate, impregnated with a 10% (w/w) solution of the
10 SPEDEK/PEKES prepared in Example 2 in 98% sulphuric acid and immediately immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 15% (w/w) solution of
15 SPEDEK/PEKES prepared in Example 2 in NMP, to 100 µm wet thickness and dried. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

20 Example 7

The procedure described in Example 6 was followed except that instead of coating with SPEDEK/PEKES in NMP, the composite membrane was coated with NMP alone, left for
25 30 minutes and dried. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite was strong and flexible.

30 Example 8

A 10% (w/w) solution of PEK™ (Grade P22, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.22 kN sm⁻²)

in 98% sulphuric acid was cast onto a glass plate to produce a 100 µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250 µm, followed by drying for 20 hours at 105 °C producing a membrane of mean thickness 50 microns. The weight ratio of ion-conducting membrane to PEKTM microporous membrane was 80:20. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

15

Example 9

A 5cm x 5cm x 50 microns sample of membrane from Example 8 and a 5cm x 5cm x 40 microns sample of the membrane from Example 3 were separately immersed in boiling deionised water (500 ml) for 60 mins, removed and dried quickly with lint-free paper to remove surface water, weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The % water-uptakes were 132% and 520% for the reinforced composite membrane and unreinforced membrane respectively, as calculated below.

30

$$\% \text{ Water-uptake} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Example 10

A 10% (w/w) solution of PES was dissolved in 98% sulphuric acid and was cast onto a glass plate to produce
5 a 100 μm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet
10 thickness of the solution of 250 μm , followed by drying for 20 hours at 105°C. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

15

Example 11

The substrate, a 10 cm by 10 cm piece of PTFE fabric was clamped to a glass plate, impregnated with a 5% (w/w)
20 solution of the SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol (30:70; w/w) and immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 5% (w/w) solution of SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol
25 (30:70; w/w), to 250 μm wet thickness and dried. The coating procedure was repeated. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and
30 flexible.

Example 12

A 7% (w/w) solution of Victrex ® PEEK™ (Grade 450G, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.45kNsm^{-2}) in methanesulphonic acid was cast onto a glass plate to produce a 100 μm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C , thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250 μm , followed by drying for 20 hours at 105°C . Compared to the wet unreinforced membrane described in Example 3 which was highly swollen and fragile, the wet composite membrane was strong and flexible.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise,

each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the
5 foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so
10 disclosed.